Preface

In recent years, several experimental and simulation results have indicated that the ion axial secular frequency in practical Paul traps differ marginally from their secular frequency in ideal traps. This shift or perturbation of ion secular frequency has been attributed to the presence of experimental and practical constraints such as geometric aberrations, space charge, dipolar excitation and damping in practical traps. In spite of clear experimental evidence for frequency perturbation, no general expression is available in literature to characterize frequency perturbation in terms of experimental conditions within the trap. The need for such expression arises in order to study not only the inter-dependence of these parameters in shifting the secular frequency but also to obtain a relationship that could be used to calibrate Paul trap mass spectrometers.

The experimental conditions in practical traps appear as non-linear parameters in the restoring term in the equation of ion motion. The equation of motion incorporating the experimental and practical constraints resembles the well-studied Duffings equation. The motivation of the present thesis will therefore be to identify a mathematical method that could be used to evaluate frequency perturbations in non-linear Paul traps when the equation of ion motion incorporates the experimental constraints.

This thesis has been divided into five chapters. In Chapter 1 we have presented the development of equation of ion motion in a pure quadrupolar field. In this chapter, the equation of motion of ions in ideal Paul traps is presented and all necessary terms for computing ideal secular frequency are introduced. Next, we have developed the equation

of motion of ions in non-ideal Paul traps. Chapter 1 also provides a brief survey of literature which have presented evidence for frequency perturbation caused by practical and experimental constraints in non-linear ion traps and the final section of this Chapter outlines the scope of the present thesis.

The scope of Chapter 2 is to understand mathematically, the perturbation of secular frequency of the ion oscillations from it's ideal value due to the presence of non-linear terms in the equation of ion motion. The motivation of this chapter is to first present the mathematical methods investigated by us namely, the method of harmonic balance and the perturbation methods for obtaining frequency shifts. Next, a brief survey of results available in mathematical literature pertinent to the circumstances encountered in describing ion motion in non-linear Paul traps are presented. This Chapter introduces the steps involved in Lindstedt – Poincare perturbation technique used in Chapter 3 for computing the shift in secular frequency of the ion oscillation. This Chapter also outlines the procedure that has to be followed in the modified Lindstedt – Poincare technique that has been used in Chapter 4 for computing the perturbation in the secular frequency of the ion oscillations.

Chapter 3 develops an algebraic expression for understanding shifts in secular frequency of the ion oscillations from it's ideal value due to the presence of non-linear terms in the equation of ion motion. We have first developed the potential function when there is hexapole and octopole superpositions due to geometric aberrations. The equation describing the ion motion inside a non-linear ion trap is developed by using this potential

function. The resulting equation of motion resembles the well-known Duffing equation with quadratic and cubic non-linearity in the restoring force term. The compatibility of Lindstedt – Poincare perturbation technique available in mathematical literature for solving this non-linear differential equations is investigated for explaining the pertinent experimental results in mass spectrometry. The results indicate that the hexapole superposition is insensitive to the sign of superposition whereas octopole superposition is sign dependent in perturbing the ion secular frequency. Further, for weak multipole superposition of the same magnitude, octopole superposition causes larger frequency shift in comparison to hexapole superposition. The dependence of secular frequency shift in mass and the axial position of the ions are also discussed. All these results are in conformity with existing experimental evidence in literature.

In Chapter 4 we have developed an expression for the perturbed secular frequency when there is field aberrations, existence of space charge, dipolar excitation and damping. A multipole superposition model incorporating hexapole and octopole superposition has been adopted to represent field aberrations. A uniform charge density distribution has been assumed for characterizing space charge. Dipolar excitation has been represented as a forcing term weighted by dipole superposition, and damping is represented in terms of collision frequency in the equation of ion motion. The final equation of motion ions resembles a forced Duffing equation with quadratic and cubic nonlinear term in the restoring force and with damping. A modified Lindstedt – Poincare technique for computing the perturbation in the ion secular frequency. The expression for perturbed frequency adequately reflects the reported experimental and simulation results.

Perturbation is sign sensitive for octopole and sign insensitive for hexapole superposition. Larger shifts occur with octopole aberrations. Perturbation of secular frequency on account of the number of ions is mass dependent. Higher masses show larger negative frequency shifts with increase in the number of ion with in the trap. Lower masses are relatively insensitive to the number of ions. Dipolar excitation is larger for lower masses than for higher masses. Damping plays a minor role in shifting the secular frequencies. The shift is negative as we increase the pressure of the bath gas. The shift in ion secular frequency with axial distance from the center of the trap shows quadratic variation.

Chapter 5 presents the highlights of our effort and directions for work which will be taken up in the laboratory.

All the references have been presented alphabetically at the end of the thesis.